2626

U.S.D.A. Research For Better Leather

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Introduction

In the last decade we have seen a great change in the hide, skin and leather economy. The postwar years brought a phenomenal increase in meat production, and the hide supply quickly rose. At the same time, the demand fell as a result of the increasing use of synthetic substitutes for leather. In 1951-52, the United States became a net exporter instead of an importer of hides.

Reflecting the changed situation, the leather research program of the Department of Agriculture was reorganized in 1953. The emphasis was shifted from conservation to utilization. The primary objective became one of stimulating the utilization of hides through developing better, more versatile, and more economical leathers to meet the challenge of the synthetics and through exploring new uses for collagen.

To achieve this objective we are conducting a broad program of research that includes studies on the composition and structure of hides and skins, the chemical modification of hide proteins, development of new tannages, improvement of processing techniques for producing leather, the dynamic measurement of the properties of leather, the evaluation of the physical chemical properties of collagen and the development of nonconventional uses for collagen.

Chemical Modification

The improvement of properties of natural products through chemical modification is well recognized by processors of wool, cotton and cellulose. We feel the same can be true for the animal proteins in hides and skins. This research has already shown that the structure of leather can be stabilized and made resistant to deterioration from perspiration and chemicals through use of polyfunctional chemicals.

For several years our Laboratory and the Quartermaster Laboratory have devoted considerable attention to studying the tanning properties of certain organic compounds known as aldehydes. A number of new aldehydes, especially dialdehydes, had become available, but no information existed about their tanning ability. (4, 15)

New Tannages

Out of these basic studies on the chemical modification of hides and hide proteins have emerged some completely new tanning agents. Dialdehyde starch (19) proved effective in shortening the time to tan sole leather; however, the current high cost has deterred its commercial adoption. Glutaraldehyde, on the other hand, is finding a growing application for the production of garment leathers with increased mellowness and for the production of shoe lining and shoe upper leathers where resistance to deterioration from perspiration and chemicals is an essential property.

Our research clearly demonstrated the versatile tanning action of glutaraldehyde and the desirable properties it imparts to leather. These studies led to the development of processes for making improved leather using glutaraldehyde alone, simultaneously in the same tan bath with chrome, and as a retannage after chrome. Such versatility, coupled with its commercial availability at reasonable cost, soon led to its commercial use in tanning by the leather industry in the U. S. (4)

Perspiration Resistant Leathers

An outstanding property that glutaraldehyde imparts to leather is resistance to deterioration from perspiration. This is true whether glutaraldehyde is used as the only tanning agent or whether it is used in combination with chrome or vegetable tans. Glutaraldehyde is much superior to formaldehyde and glyoxal in conferring perspiration resistance.

The notable resistance to perspiration of this leather has led to new applications. It has caught on in work shoe leather, and field tests have substantiated laboratory tests. Work shoes made with leather tanned with glutaraldehyde alone or in combination with chrome have given excellent service to workers in dairy barns, paper mills, cement plants, and gasoline stations, where perspiration, alkali, and alkaline cleansing agents rapidly deteriorate leather. Glutaraldehyde-chrome combination leathers are now available in work shoes at the retail level.

More recently, glutaraldehyde is finding application as a retannage for white shoe upper leathers to give them greater perspiration resistance.

Launderable Shearlings

Another property glutaraldehyde imparts to leather is improved resistance to hot soap solution. This property suggested the use of this tanning agent for the production of "easy care" shearlings. The use of shearlings as hospital bed pads has been known to reduce the incidence of bed sores among bedridden patients. However, the extreme care required to prevent damage to the leather during cleaning and sanitizing discouraged their extensive use. Workers in Australia recently reported on the washability of shearlings tanned with high amounts of chromium salts. Our studies have shown that shearlings can be produced where the pelt would not shrink or harden on repeated laundering in warm soapy water. Launderability was imparted by tanning with 15% of commercial glutaraldehyde solution or by lesser amounts if fortified with a small amount of chrome. Work with shearlings is complicated by the fact that wool is present in addition to the skin. Although glutaraldehyde stabilizes the skin towards washing, it does not prevent the wool from matting. This does not appear to be a detriment to the application of shearlings as hospital bed pads. However, solution of this problem could enhance the utility of shearlings and open new markets. (7)

Shearlings tanned with glutaraldehyde retain their water absorption property and keep the skin surface dry by absorbing and removing liberated perspiration. This property gives shearlings a practical advantage over synthetics that are being promoted for hospital bed pads.

The biggest benefit of this development accrues in the comeback of shearlings in paint rollers. Water-based paints with their alkaline emulsifiers almost eliminated this market for shearlings. This is an excellent example of how the improvement in the properties of a natural product permits it to compete more effectively with synthetic substitutes.

Color-Fast Leathers

The successful results with shearlings prompted us to explore the possibility of extending this development to other areas and applications. Chrome-tanned cabretta leathers retanned with glutaraldehyde were tested in golf gloves. These tests proved that washability coupled with resistance to perspiration damage produced a superior product. However, we found we could not stop there. If we were to have washable gloves, we needed color-fast dyes, and this has started us on a study on the application of reactive dyestuffs to leather. (18)

Color-fastness may have even greater significance in shoe upper leathers. Leathers that stain through bleeding of the dye constitute a source of annoyance to the consumer. Can the leather industry afford to ignore the problem in the face of color-fast substitutes?

Water Resistance

Footwear resistant to penetration of liquid water offer certain advantages, and considerable effort has been devoted to the production of leathers with this property. Silicones, chrome salts of perfluoro acids, alkenyl succinic acid and stearato chromic chloride have been used to make leather resistant to water penetration. It has been accepted that the fat content should be kept at a low level, that the types of fat liquor used be emulsified oils or solvent base fat liquors and that highly sulfated oils tend to act as wetting agents and could have a decided detrimental influence on water resistance. (5, 6)

Our approach was to capitalize on the studies of others who suggested that the alkenyl succinic acids (ASA) offered promise as lubricants for preparing leather to be given water-repellent treatments. Our studies showed that emulsions of ASA or ASA mixed with raw oils suitable for use in conventional fat-liquoring operations could be produced through the use of water-soluble, high-boiling, polar compounds; such as, tetrahydrofurfuryl alcohol or butyl carbitol, as dispersion aids. (9)

Leathers fat-liquored in this manner were quite receptive to silicone and the other water-repellent systems. Experimental data indicated that acceptable water resistance could be obtained with lower levels of water-repellent treatment than on ordinary leather substrates. Glutaraldehyde retannage of chrome stock was also helpful in making the substrate more receptive to water-repellent treatments. (5, 9)

Dynamic Measurement of Properties

Leather derives much of its value from its performance under dynamic conditions of stress and strain. Its ability to absorb shock, withstand stress, regain its dimensions and to conform to shape constitutes a unique set of properties. However, these characteristics cannot always be determined or predicted from tests at ultimate stress or at failure.

We are studying the physics of leather structure under dynamic conditions by means of a nondestructive tester designed specifically for this purpose. The instrument imparts a sinusoidal compressive force, and the resonant frequency is measured. From this the relative stiffness (apparent modulus of compression) is calculated. When the resonant frequencies are measured over the entire intact side, a pattern is obtained which shows the variability of the mechanical properties within the side of leather. This test indicated that the butt and backbone areas contained the regions of highest stiffness, and the belly and neck areas have the most flexible regions. However, when an attempt was made to correlate these properties with results obtained by other methods of test, there was disagreement. Flexure and torsion modulus gave a reverse trend. These tests showed a high modulus (stiffness) in the neck and belly areas and low modulus (flexibility) in the butt-backbone areas. (13)

We feel that these results are real and the controversial observations reflect some structural characteristic of leather that we do not completely understand. This may explain why sorters do not always agree on the quality of a side of leather from its appearance, feel and texture. We are faced with the problem of resolving these differences and establishing a correlation with actual use performance.

Stiffness of Work Glove Leathers

Our interest in the physical properties of leather led us to explore the possibility of developing an objective test for measuring the stiffness of work glove leather. The torsion test was selected because of its simplicity. In order to establish limits or ranges, we procured sides of cattlehide work glove leather to represent varying degrees of stiffness, including soft, moderately soft, and firm. Most individuals evaluating these sides had no difficulty in determining the firm side, but there was some disagreement in rating the soft and moderately soft sides in proper sequence.

Our next step was to make gloves from these sides in order to establish whether the characteristics of the sides would carry through into the finished item. The results were most surprising. We found that the gloves cut from the neck areas were the stiffest, while those from the butt areas were the softest (most flexible). Actually the glove cut from the neck area of the side graded soft was stiffer than the glove cut from the butt area of the side graded firm. Also, some individuals had difficulty in distinguishing the differences in stiffness among the gloves cut from the butt areas of the sides with the three degrees of firmness.

On the basis of this test, we would suggest that tanners of cattle sides for work gloves segment the hides by removing a double shoulder. The double shoulders could be processed into other type leathers while the remaining part of the hide would give a more desirable leather with greater uniformity of softness.

Hide Structure

Since leather is utilized as a 3-dimensional sheet, our approach to the composition of hide has been to study the distribution of components stratigraphically in layers. These investigations have shown that the components of fresh skins are not evenly distributed through the thickness of a skin. When sections of equal thickness were cut and their dry weight determined, there was only about one-half as much dry matter in the grain layer as in the corium(10). The distribution of nitrogen content (a measure of protein) and of hydroxyproline (a measure of collagen) gave pictures similar to that of the dry weight[11]. The distribution of the lipid components also shows stratification within the hide. (1)

The jelly-like materials of high moisture content (ground substance and cellular tissue) which fill the spaces between the fibers are removed by the pretanning processes. These studies indicate, therefore, that the grain layer of the resulting leather will have a more open structure than that of the corium. The porous matrix formed by this structural arrangement of fibers gives leather many of its unique properties. It gives leather its ability to transmit water vapor and its high resistance to flexural fatigue. However, this should also be of great interest to the tanner. He can take advantage of the porous nature to control and modify the texture and other properties of leather by introducing polymers and other chemical modifiers. (8, 12)

Hide Defects

In our investigations of the architecture of hides and leather, we have found that the microscope is a powerful tool for elucidating the structural features. For example, in studying veininess (a costly defect in glazed calfskin leather) we found that the surface defect was a manifestation of the void space surrounding blood vessels. When the surrounding fiber bundles are pushed into the voids by mechanical treatments, indentations appear on the surfaces of the leather which are characterized by differences in glossiness of the finish. These observations suggested that the defect could be corrected if the void spaces could be filled. Some progress toward alleviating the condition has been made by application of zirconium retannage or by resin impregnation. (2, 14)

Another application has been to the study of the pulpy butt defect. The defect proved to be characterized by a vertical arrangement of the fibers. (3) "Vertical fiber" consists of an abnormal arrangement of corium fiber bundles, in a direction nearly vertical to the grain surface. Upper leathers made from the defective hides can usually be recognized by their characteristic pulpy texture and inferior strength. The basic cause has not been determined, but the defect is also known to occur in Australia, Argentina and Great Britain. Thus the problem is not unique to domestic hides.

When we learned that the Tanners' Council Laboratory was also studying the problem, we decided to pool our efforts. They recently completed a large-scale study exploring various factors to determine the cause and incidence of the vertical fiber defect. The results indicate that the defect is not caused by poor curing or tanning but is inherent to the hide. The fibers in the affected area are loosely woven and perpendicular to the hide surface rather than tightly woven and parallel to the hide surface as they should be. This accounts for the lack of tensile strength. Such hides often have a high fat content. Usually the weakness occurs in only a small area of the hide. Thick, heavy Hereford hides have the defect more often than other kinds of hides, and it probably occurs in only 10% or less of the heavy Hereford hides. (16)

Our more recent efforts are directed to the characterization of damage caused to hides by insects, and to sheepskins by cockle, and to the evaluation of the changes induced in the skin structure by freezebranding.

Segmentation of Hides

Probably the greatest potential for improving the quality and uniformity of leather lies in segmentation of hides. The use of rectangular shaped rawstock offers the possibility of gaining economic advantages from development of through-put equipment, savings in processing chemicals and improvement of over-all tannery efficiency. However, the idea to square off cattlehides by removing the less desirable leather-making areas is not finding ready acceptance. Although economic evaluations indicate that a tanner would be money ahead to throw away the trimmings, there is a great psychological reluctance to discard material that costs 12 to 18 cents per pound. (17)

The segmentation of cattlehides has the potential of making about 100 million pounds of dry weight collagen available annually. Alternative markets for this raw material would do much to improve the economics of hide utilization and leather processing. Our research is aimed to develop new outlets in the edible field. To accomplish this, we are studying the properties of collagen and its behavior in different chemical environments. This includes investigations of soluble collagen in solution and in its fibrous form after regeneration.

Since soluble collagen forms only a fraction of the total skin collagen, we are devoting considerable effort to develop processes for dispersing and rearranging the insoluble form. As a result of this research, we have learned how to comminute a hide and to disperse the fibrous network (20). We are now evaluating the properties of such dispersions to determine their most profitable application.

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